Supporting Information for:

Air-Assisted Addition of Grignard Reagents to Olefins. A Simple Protocol for Three-Component Coupling Process Yielding Alcohols

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General. ^1H and ^{13}C NMR spectra were taken on a Varian Gemini-300 spectrometer at 300 and 75 MHz, respectively. CDCl_3 was used as the solvent. Chemical shifts are reported in parts per million shift (δ value) from Me_4Si (δ 0 ppm for ^1H) or based on the middle peak of the solvent (CDCl_3) (δ 77.00 ppm for ^{13}C NMR) as an internal standard. Signal patterns are indicated as br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (J) are given in Hertz. Infrared (IR) spectra were recorded on a JASCO A-100 spectrometer and are reported in wave numbers (cm^{-1}). (Trimethylsilyl)- and (dimethylphenylsilyl)methylmagnesium chlorides were prepared in Et_2O as an approximately 1 M solution from the corresponding chlorides and magnesium turnings by the usual procedure, titrated, and stocked under an argon atmosphere. Air for reactions was dried with SICAPENT (E. Merck). Dry THF and ether were purchased from Kanto Chemicals Co. (Japan). Chemicals were purified or dried in a standard manner, if necessary. Although we could not detect the formation of hydroperoxide after the aerial oxidation, its presence in a crude reaction mixture should be carefully checked by KI-starch paper, etc., particularly in medium to large-scale preparations.

General Procedure for O_2 -Assisted Grignard Addition. 4-(Trimethylsilyl)-2-phenyl-2-butanol (16). A 10-mL flask in the shape of a test tube was equipped with a balloon filled with

dry air. To this flask were charged dry air and a neat sample of α -methylstyrene (**9**) (0.028 mL, 0.200 mmol), followed by $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (**7**) (1.15 M in Et_2O , 0.520 mL, 0.600 mmol), at room temperature under stirring. After the mixture was stirred under dry air overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (3% ethyl acetate in hexane) to afford the title compound (40 mg, 90%) as a colorless oil.

^1H NMR δ 0.08 (s, 9H), 0.28 (d/t, $J = 4.8, 12.6$ Hz, 1H), 0.43 (d/t, $J = 4.8, 12.6$ Hz, 1H), 1.55 (s, 3H), 1.69-1.88 (m, 2H), 1.84 (s, 1H), 7.24 (d/t, $J = 1.5, 7.5$ Hz, 1H), 7.32-7.44 (m, 4H).

^{13}C NMR δ 1.01, 10.07, 29.62, 38.09, 75.32, 124.92, 126.42, 128.08, 128.09.

IR (neat) 3447 (OH), 3025, 2960, 1447, 1261, 1107, 1021, 863, 802, 700 cm^{-1} .

Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{OSi}$: C, 70.21; H, 9.97. Found: C, 70.20; H, 9.90.

4-(Trimethylsilyl)-2-phenyl-2-butanol (16) Prepared in a 2.5-mmol Scale. A 30-mL, round-bottomed flask was equipped with a balloon filled with dry air. To this flask were charged dry air and a neat sample of α -methylstyrene (**9**) (0.33 mL, 2.5 mmol), followed by $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (**7**) (0.91 M in Et_2O , 8.2 mL, 7.5 mmol), at room temperature under stirring. After the mixture was stirred under dry air for 3 days, the reaction was terminated by the addition of water (7.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, which was checked by wet KI-starch paper, showing the absence of peroxides. The crude product was chromatographed on silica gel (3% ethyl acetate in hexane) to afford the title compound (400 mg, 72%) as a colorless oil.

Peroxides, which may be produced in place of the alcohol or from the solvent, should be removed by the treatment with an appropriate reducing agent [Wakefield, B. J. *Organomagnesium Methods in Organic Synthesis*; Academic Press: London, 1995; pp 197-199.

Nakamura E.; Inubushi, T.; Aoki, S.; Machii, D. *J. Am. Chem. Soc.* **1991**, *113*, 8980-8982.
Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd Ed.; Pergamon Press: Oxford, 1980; pp 259-260 and pp 426-427]. For analysis of peroxides, see: (NMR) Klement, I.; Knochel, P. *Synlett* **1995**, 1113-1114; (iodometrical titration) Abraham, M. H. *J. Chem. Soc.* **1960**, 4130-4135.

4,4-Dimethyl-2-phenyl-2-pentanol (12). This was prepared from **9** and a 2.0 M ether solution of *t*-BuMgCl (**3**) according to the general procedure.

¹H NMR δ 0.81 (s, 9H), 1.55 (s, 3H), 1.87 (d, *J* = 12.0 Hz, 1H), 1.81 (d, *J* = 12.0 Hz, 1H), 2.15 (s, 1H), 7.24-7.45 (m, 5H).

5-Methyl-2-phenyl-4-hexen-2-ol (13). This was prepared from **9** and a 0.50 M THF solution of CMe₂=CHMgBr (**4**) according to the general procedure.

¹H NMR δ 1.54 (s, 3H), 1.61 (s, 3H), 1.69 (s, 3H), 1.80 (s, 1H), 2.54 (d, *J* = 8.1 Hz, 2H), 5.00 (t, *J* = 8.1 Hz, 1H), 7.21-7.47 (m, 5H).

¹³C NMR δ 26.03, 29.80 (2 peaks), 42.42, 74.43, 118.76, 124.81, 126.44, 128.07, 136.63, 148.07.

IR (neat) 3421 (OH), 2967, 2919, 1654, 1448, 1376, 1067, 1025, 700 cm⁻¹.

Anal. Calcd for C₁₃H₁₈O: C, 82.06; H, 9.53. Found: C, 81.68; H, 9.34.

4-Methyl-2-phenyl-4-penten-2-ol (14). This was prepared from **9** and a 0.50 M THF solution of CH₂=CH(Me)MgBr (**5**) according to the general procedure.

¹H NMR δ 1.39 (s, 3H), 1.56 (s, 3H), 1.74 (s, 1H), 2.52 (d, *J* = 13.2 Hz, 1H), 2.64 (d, *J* = 13.2 Hz, 1H), 4.74 (d, *J* = 0.9 Hz, 1H), 4.89 (d, *J* = 0.9 Hz, 1H), 7.19-7.46 (m, 5H).

¹³C NMR δ 24.16, 29.22, 52.00, 71.51, 115.62, 125.52, 126.46, 128.02, 147.92, 150.37.

IR (neat) 3447 (OH), 3044, 2926, 2855, 1675, 1448, 1375, 1069, 701 cm⁻¹.

Anal. Calcd for C₁₂H₁₆O: C, 81.77; H, 9.15. Found: C, 81.75; H, 9.10.

1,2-Diphenyl-2-propanol (15). According to the general procedure, to a stirred neat sample of α -methylstyrene (**9**) (24 mg, 0.200 mmol) was added PhMgBr (**6**) (1.00 M in THF, 0.600 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.50 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ¹H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (32 mg, 75 %) as a colorless oil.

¹H NMR δ 1.58 (s, 3H), 2.02 (s, 1H), 3.05 (d, *J* = 13.2 Hz, 1H), 3.16 (d, *J* = 13.2 Hz, 1H), 7.21-7.42 (m, 10H).

¹³C NMR δ 29.33, 50.43, 74.63, 115.27, 120.67, 124.95, 126.66, 126.58, 128.06, 129.63, 130.58.

IR (neat) 3372 (OH), 3040, 2968, 1595, 1499, 1473, 1230, 1069, 812, 754, 700 cm⁻¹.

Anal. Calcd for C₁₅H₁₆O: C, 84.87; H, 7.60. Found: C, 84.43; H, 8.00.

Control Experiment in Reference 8. Formation of 4-(Trimethylsilyl)-2-phenyl-2-butanol (16) from Me₃SiCH₂Li. According to the general procedure, to a stirred neat sample of α -methylstyrene (**9**) (0.028 mL, 0.200 mmol) was added Me₃SiCH₂Li (1.0 M in pentane, 0.600 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (19 mg, 42%) as a colorless oil.

Note that, when this reaction was carried out under pure argon with complete exclusion of O₂, the olefin was quantitatively recovered, confirming that carbolithiation to the olefin was negligible.

Control Experiment in Reference 8. Formation of 4-(Trimethylsilyl)-2-phenyl-2-butanol (16) from Me₃SiCH₂ZnCl. To a stirred solution of ZnCl₂ (1.0 M in Et₂O, 0.600 mL, 0.600 mmol) was added Me₃SiCH₂Li (1.0 M in pentane, 0.600 mL, 0.600 mmol) at room temperature under argon and the mixture was stirred at the same temperature for 30 min. α -Methylstyrene (**9**) (0.028 mL, 0.200 mmol) was added to this solution of Me₃SiCH₂ZnCl, and the argon was replaced by dry air. After the mixture was stirred under dry air overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, which was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (6 mg, 13%) as a colorless oil.

4-(Dimethylphenylsilyl)-2-phenyl-2-butanol (17). According to the general procedure, to a stirred neat sample of α -methylstyrene (**9**) (0.028 mL, 0.200 mmol) was added PhMe₂SiCH₂MgCl (**8**) (1.08 M in Et₂O, 0.556 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ¹H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (42 mg, 74%) as a colorless oil.

¹H NMR δ 0.24 (s, 3H), 0.25 (s, 3H), 0.50-0.60 (m, 1H), 0.66-0.77 (m, 1H), 1.53 (s, 3H), 1.72-1.91 (m, 2H), 3.50 (s, 1H), 7.22-7.28 (m, 1H), 7.31-7.47 (m, 8H), 7.57-7.64 (m, 1H).

¹³C NMR δ -3.30, -3.19, 9.16, 29.70, 37.90, 75.33, 124.92, 126.45, 127.87, 128.09, 128.87, 133.84, 138.85, 147.60.

IR (neat) 3386 (OH), 3069, 2959, 2862, 1427, 1249, 1115, 1058, 835, 728, 700 cm⁻¹.

Anal. Calcd for C₁₈H₂₄OSi: C, 76.00; H, 8.50. Found: C, 76.40; H, 8.33.

(E)-1-Methyl-4-(1-methyl-1,3-butadienyl)benzene (24). This was prepared according to the following literature [Ikeda, Y.; Ukai, J.; Ikeda, N.; Yamamoto, H. *Tetrahedron* **1987**, *43*, 723-730]. ¹H NMR δ 2.18 (s, 3H), 2.38 (s, 3H), 5.04-5.10 (m, 2H), 6.45 (d/d, *J* = 1.6, 12.6 Hz, 1H), 6.78 (d/d/d, *J* = 11.4, 12.6, 16.0 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H).

1-[2-(1-Methoxy-2-methylpropyl)phenyl]-3-(trimethylsilyl)-1-propanol as a 70:30 Mixture of Diastereoisomers (25). According to the general procedure, to a stirred neat sample of 1-(1-methoxy-2-methylpropyl)-2-vinylbenzene (**18**) (38 mg, 0.200 mmol) was added Me₃SiCH₂MgCl (**7**) (1.15 M in Et₂O, 0.520 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo* to give a crude oil, ¹H NMR analysis of which revealed that this product is a 70:30 mixture of diastereoisomers. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (32 mg, 75 %, a 70:30 mixture of inseparable diastereoisomers) as a colorless oil.

¹H NMR δ -0.02 (s, 9H), 0.36-0.49 (m, 1H), 0.67-0.82 (m, 1H), 0.75 (d, *J* = 6.6 Hz, 3H × 0.70), 0.81 (d, *J* = 6.6 Hz, 3H × 0.30), 1.03 (d, *J* = 6.6 Hz, 3H × 0.30), 1.05 (d, *J* = 6.6 Hz, 3H × 0.70), 1.80 (m, 2H), 1.88-2.04 (m, 1H), 1.92 (s, 1H), 3.16 (s, 3H × 0.30), 3.18 (s, 3H × 0.70), 4.11 (d, *J* = 7.8 Hz, 1H), 4.93-5.01 (m, 1H), 7.28-7.51 (m, 4H).

¹³C NMR δ -1.86, -1.84, 1.00, 12.95, 13.24, 18.55, 18.80, 19.61, 19.97, 32.56, 33.04, 34.56, 35.06, 56.82, 57.07, 71.89, 71.95, 85.99, 86.23, 125.39, 125.80, 127.22, 127.31, 127.60, 127.98, 138.14, 138.57, 142.80, 142.86 for a 70:30 mixture of diastereoisomers. These peaks may be overlapping due to a 70:30 mixture of diastereoisomers.

IR (neat) 3437 (OH), 3066, 2954, 2813, 1449, 1385, 1249, 1094, 836, 691 cm⁻¹ for a 70:30 mixture of diastereoisomers.

Anal. Calcd for. C₁₇H₂₂O₂Si: C, 69.33; H, 10.27. Found: C, 69.01; H, 9.99 for a 70:30 mixture of diastereoisomers.

1-[2-(1-Hydroxyethyl)phenyl]-3-(trimethylsilyl)-1-propanol as an 86:14 Mixture of Diastereoisomers (26). According to the general procedure, to a stirred neat sample of 1-(2-vinylphenyl)ethanol (**19**) (30 mg, 0.200 mmol) was added $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (**7**) (1.15 M in Et_2O , 0.696 mL, 0.800 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (3.0 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which revealed that this product is an 86:14 mixture of diastereoisomers. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (30 mg, 68%, 86:14 mixture of inseparable diastereoisomers) as a colorless oil.

Major product.

^1H NMR δ 0.06 (s, 9H), 0.38-0.46 (m, 1H), 0.64-0.86 (m, 1H), 1.54 (d, $J = 6.6$ Hz, 3H), 1.74-1.84 (m, 2H), 1.95 (s, 1H), 2.05 (s, 1H), 4.88 (t, $J = 6.9$ Hz, 1H), 5.26 (q, $J = 6.3$ Hz, 1H), 7.26-7.31 (m, 2H), 7.39-7.42 (m, 1H), 7.50-7.53 (m, 1H).

^{13}C NMR δ 1.82, 13.07, 24.52, 32.88, 66.60, 73.92, 125.57, 126.47, 127.72, 127.87, 140.89, 142.64 for an 86:14 mixture of diastereoisomers.

IR (neat) 3430 (OH), 3022, 2960, 1430, 1238, 1100, 836, 693 cm^{-1} for an 86:14 mixture of diastereoisomers.

Anal. Calcd for. Found: $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Si}$: C, 66.61; H, 9.58. Found: C, 66.51; H, 9.60 for an 86:14 mixture of diastereoisomers.

Minor product.

^1H NMR δ 0.06 (s, 9H), 0.38-0.46 (m, 1H), 0.64-0.86 (m, 1H), 1.54 (d, $J = 6.6$ Hz, 3H), 1.74-1.84 (m, 2H), 1.96 (s, 1H), 2.08 (s, 1H), 4.91 (t, $J = 6.9$ Hz, 1H), 5.26 (q, $J = 6.3$ Hz, 1H), 7.26-7.31 (m, 2H), 7.39-7.42 (m, 1H), 7.50-7.53 (m, 1H).

2-(5-Methylfuran-2-yl)-4-(trimethylsilyl)-2-butanol (27). This was prepared according to the general procedure.

^1H NMR δ 0.08 (s, 9H), 0.29-0.48 (m, 2H), 1.59 (s, 3H), 1.76-1.82 (m, 2H), 1.90 (s, 1H), 2.27 (s, 3H), 5.87 (br d, $J = 3.0$ Hz, 1H), 6.04 (br d, $J = 3.0$ Hz, 1H).

^{13}C NMR δ -1.94, 10.51, 13.51, 25.69, 35.68, 72.42, 105.41, 105.75, 151.03, 157.65.

IR (neat) 3432 (OH), 2953, 1559, 1248, 1099, 1021, 862, 797, 691 cm^{-1} .

Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_2\text{Si}$: C, 63.66; H, 9.80. Found: C, 63.23; H, 9.90.

A 50:50 Regioisomeric Mixture of (*E*)-1-(Trimethylsilyl)-4-undecen-3-ol and (*E*)-1-(Trimethylsilyl)-3-undecen-5-ol (28). According to the general procedure, to a stirred neat sample of 1,3-decadiene (**21**) (28 mg, 0.200 mmol) was added $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (**7**) (1.15 M in Et_2O , 0.520 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil, ^1H NMR analysis of which revealed that this product is a 50:50 mixture of regioisomers. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (32 mg, 65 %, a 50:50 mixture of inseparable regioisomers) as a colorless oil.

(*E*)-1-(Trimethylsilyl)-4-undecen-3-ol.

^1H NMR δ 0.05 (s, 9H), 0.47-0.58 (m, 2H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.20-1.29 (m, 10H), 1.61 (s, 1H), 1.99-2.07 (m, 2H), 4.02 (q, $J = 6.6$ Hz, 1H), 5.43 (d/d, $J = 6.6, 15.0$ Hz, 1H), 5.64 (t/d, $J = 6.3, 15.0$ Hz, 1H).

(*E*)-1-(Trimethylsilyl)-3-undecen-5-ol.

^1H NMR δ 0.05 (s, 9H), 0.47-0.58 (m, 2H), 0.88 (t, $J = 6.9$ Hz, 3H), 1.20-1.29 (m, 10H), 1.61 (s, 1H), 1.99-2.07 (m, 2H), 3.94 (q, $J = 6.6$ Hz, 1H), 5.40 (d/d, $J = 6.6, 15.6$ Hz, 1H), 5.68 (t/d, $J = 6.3, 15.6$ Hz, 1H).

^{13}C NMR δ -1.79, -1.65, 1.01, 11.95, 14.10, 16.16, 22.66, 25.50, 29.16, 29.19, 29.29, 29.44, 29.57, 31.55, 31.87, 32.23, 37.35, 73.20, 75.51, 131.55, 132.60, 132.65, 134.92 for a 50:50 mixture of regioisomers. These peaks may be overlapping due to a 50:50 mixture of regioisomers.

IR (neat) 3345 (OH), 2960, 2925, 2855, 1540, 1248, 968, 862, 836, 690 cm^{-1} for a 50:50 mixture of regioisomers.

Anal. Calcd for $\text{C}_{14}\text{H}_{30}\text{OSi}$: C, 69.35; H, 12.47. Found: C, 69.05; H, 12.66 for a 50:50 mixture of regioisomers.

A 50:50 Regioisomeric Mixture of 1-(1-Cyclohexenyl)-3-(trimethylsilyl)-1-propanol (A) and (Z)-2-[3-(Trimethylsilyl)propylidene]-1-cyclohexanol (B) (29). This was prepared according to the general procedure.

^1H NMR δ 0.06 (s, 9H), 0.28-0.39 (m, $1\text{H} \times 0.5$), 0.45-0.59 (m, $1\text{H} \times 0.5 + 2\text{H} \times 0.5$), 1.47-1.66 (m, $6\text{H} \times 0.5 + 6\text{H} \times 0.5$), 1.80 (s, 1H), 1.85-2.07 (m, 2.5H), 1.85-2.07 (m, $2\text{H} \times 0.5$), 2.38 (q, $J = 6.9$ Hz, $1\text{H} \times 0.5$), 3.86 (t, $J = 6.6$ Hz, $1\text{H} \times 0.5$, **A**), 4.05 (m, $1\text{H} \times 0.5$, **B**), 5.37 (t, $J = 7.2$ Hz, $1\text{H} \times 0.5$, **B**), 5.64 (br s, $1\text{H} \times 0.5$, **A**).

^{13}C NMR δ -1.80, -1.59, 12.15, 17.29, 21.08, 22.64, 22.75, 23.26, 24.98, 25.67, 27.14, 28.85, 35.92, 73.73, 79.15, 123.64, 124.46, 139.48 for a 50:50 mixture of regioisomers. These peaks may be overlapping due to a 50:50 mixture of regioisomers.

IR (neat) 3361 (OH), 2960, 2929, 2861, 1437, 1260, 1107, 1018, 834, 813, 699 cm^{-1} for a 50:50 mixture of regioisomers.

Anal. Calcd for $\text{C}_{12}\text{H}_{24}\text{OSi}$: C, 67.86; H, 11.39. Found: C, 67.56; H, 11.72 for a 50:50 mixture of regioisomers.

The olefinic stereochemistry of **B** proved to be defined, but its structure (*E* or *Z*) has not been determined.

A 50:50 Regioisomeric Mixture of 3-Methyl-1-phenyl-5-(trimethylsilyl)-2-penten-1-ol and (*E*)-3-Methyl-1-phenyl-5-(trimethylsilyl)-1-penten-3-ol (30). This was prepared according to the general procedure.

(*E*)-3-Methyl-1-phenyl-5-(trimethylsilyl)-2-penten-1-ol.

^1H NMR δ 0.07 (s, 9H), 0.60-0.66 (m, 2H), 1.81 (s, 3H), 1.60 (br s, 1H), 2.01 (symmetrical m, 2H), 5.44 (d/m, $J = 8.7$ Hz with fine splitting due to allylic coupling, 1H), 5.49 (br d, $J = 8.7$ Hz, 1H), 7.20-7.41 (m, 5H). NOESY experiments showed the correlation between the protons at δ 1.81 ppm ($\text{C}=\text{CCH}_3$) and at δ 5.49 ppm ($\text{CH}(\text{OH})$). Thus, the stereochemistry has been confirmed.

(*E*)-3-Methyl-1-phenyl-5-(trimethylsilyl)-1-penten-3-ol.

^1H NMR δ 0.07 (s, 9H), 0.48-0.66 (m, 2H), 1.38 (s, 3H), 1.56-1.62 (m, 2H), 1.60 (br s, 1H), 6.26 (d, $J = 16.2$ Hz, 1H), 6.58 (d, $J = 16.2$ Hz, 1H), 7.20-7.41 (m, 5H).

^{13}C NMR δ -1.88, -1.81, 1.00, 10.16, 14.63, 16.58, 27.59, 33.59, 36.91, 70.74, 73.90, 125.81, 125.84, 126.35, 127.22, 127.31, 128.43, 128.54, 136.59, 137.04, 141.55, 144.32 for a 50:50 mixture of regioisomers. These peaks may be overlapping because of a 50:50 mixture of regioisomers.

IR (neat) 3393 (OH), 3025, 2954, 2919, 1442, 1247, 862, 837, 692 cm^{-1} for a 50:50 mixture of regioisomers.

Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{OSi}$: C, 72.52; H, 9.74. Found: C, 72.70; H, 9.70 for a 50:50 mixture of regioisomers.

(*E*)-2-(*p*-Tolyl)-6-methyl-3,6-heptadien-2-ol (31). According to the general procedure, to a stirred neat sample of (*E*)-1-methyl-4-(1-methyl-1,3-butadienyl)benzene (**24**) (24 mg, 0.200 mmol) prepared above was added $\text{CH}_2=\text{CH}(\text{Me})\text{MgBr}$ (**5**) (0.50 M in THF, 1.20 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR

spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (29 mg, 68 %) as a colorless oil.

^1H NMR δ 1.64 (s, 3H), 1.72 (s, 3H), 1.94 (s, 1H), 2.34 (s, 3H), 2.75 (d, $J = 6.9$ Hz, 2H), 4.70 (s, 1H), 4.74 (s, 1H), 5.68 (t/d, $J = 6.9, 15.6$ Hz, 1H), 5.84 (d, $J = 15.6$ Hz, 1H), 7.14 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.4$ Hz, 2H).

^{13}C NMR δ 20.96, 22.47, 29.84, 40.65, 74.27, 110.85, 125.10, 126.18, 128.84, 136.44, 138.81, 144.14, 144.46.

IR (neat) 3402 (OH), 3038, 2969, 2927, 1654, 1458, 1262, 1083, 889, 818, 674 cm^{-1} .

Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}$: C, 83.28; H, 9.32. Found: C, 83.46; H, 9.10.

1-(Dimethylphenylsilyl)-4-pentadecyn-3-ol (35). According to the general procedure, to a stirred neat sample of 1-tetradecen-3-yne (**32**) (39 mg, 0.200 mmol) was added $\text{PhMe}_2\text{SiCH}_2\text{MgCl}$ (**8**) (0.93 M in Et_2O , 0.645 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products such α,β -unsaturated ketones or an allenyl alcohol. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (51 mg, 71%) as a colorless oil.

^1H NMR δ 0.03 (s, 6H), 0.86-0.94 (symmetrical m, 2H), 0.90 (t, $J = 6.9$ Hz, 3H), 1.20-1.45 (m, 14H), 1.52 (quintet, $J = 6.9$ Hz, 2H), 1.62-1.73 (symmetrical m, 2H), 1.86 (br s, 1H), 2.21 (d/t, $J = 1.8, 6.9$ Hz, 2H), 4.29 (t/t, $J = 1.8, 6.3$ Hz, 1H), 7.34-7.39 (m, 3H), 7.50-7.56 (m, 2H).

^{13}C NMR δ -3.15 (2 peaks), 10.75, 14.08, 18.65, 22.65, 28.68, 28.85, 29.12, 29.29, 29.53, 29.57, 31.87, 32.55, 64.90, 81.11, 85.71, 127.73, 128.87, 133.51, 138.88.

IR (neat) 3448 (OH), 3069, 3049, 2926, 2854, 2229, 1467, 1427, 1377, 1336, 1248, 1178, 1114, 1046, 1012, 869, 838, 822, 780, 728, 699 cm^{-1} .

Anal. Calcd for $C_{23}H_{38}OSi$: C, 77.03; H, 10.68. Found: C, 77.07; H, 10.76.

3-Methyl-1-(trimethylsilyl)-4-pentadecyn-3-ol (36) According to the general procedure, to a stirred neat sample of 2-methyl-1-tetradecen-3-yne (**33**) (41 mg, 0.200 mmol) was added Me_3SiCH_2MgCl (**7**) (0.91 M in Et_2O , 0.659 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by 1H NMR spectroscopy did not show the presence of any isomeric products such α,β -unsaturated ketones or an allenyl alcohol. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (43 mg, 70%) as a colorless oil.

1H NMR δ 0.00 (s, 9H), 0.60-0.70 (symmetrical m, 2H), 0.87 (t, $J = 6.8$ Hz, 3H), 1.16-1.41 (m, 14H), 1.43 (s, 3H), 1.48 (quintet, $J = 6.9$ Hz, 2H), 1.53-1.62 (symmetrical m, 2H), 1.94 (br s, 1H), 2.18 (t, $J = 6.9$ Hz, 2H).

^{13}C NMR δ -1.86, 11.09, 14.07, 18.58, 22.65, 28.74, 28.81, 29.12, 29.30, 29.34, 29.57, 29.55, 31.87, 38.34, 69.54, 83.85, 84.04.

IR (neat) 3388 (OH), 2954, 2927, 2855, 2238, 1466, 1369, 1259, 1248, 1186, 1157, 1070, 1024, 935, 918, 863, 836, 758, 691 cm^{-1} .

Anal. Calcd for $C_{19}H_{38}OSi$: C, 73.47; H, 12.33. Found: C, 73.65; H, 12.39.

1-(Dimethylphenylsilyl)-3-methyl-4-pentadecyn-3-ol (37). According to the general procedure, to a stirred neat sample of 2-methyl-1-tetradecen-3-yne (**33**) (41 mg, 0.200 mmol) was added $PhMe_2SiCH_2MgCl$ (**8**) (0.93 M in Et_2O , 0.645 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil. Careful

analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products such α,β -unsaturated ketones or an allenyl alcohol. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (57 mg, 76%) as a colorless oil.

^1H NMR δ 0.03 (s, 6H), 0.90 (t, $J = 6.9$ Hz, 3H), 0.91-1.00 (symmetrical m, 2H), 1.20-1.42 (m, 14H), 1.44 (s, 3H), 1.50 (quintet, $J = 6.9$ Hz, 2H), 1.58-1.67 (symmetrical m, 2H), 1.95 (br s, 1H), 2.19 (t, $J = 6.9$ Hz, 2H), 7.33-7.39 (m, 3H), 7.49-7.57 (m, 2H).

^{13}C NMR δ -3.16 -3.12, 10.18, 14.08, 18.58, 22.66, 28.75, 28.84, 29.13, 29.30, 29.37, 29.54, 29.58, 31.88, 38.21, 69.50, 83.89, 83.99, 127.74, 128.86, 133.54, 138.96.

IR (neat) 3397 (OH), 3069, 3049, 2954, 2927, 2854, 2239, 1456, 1427, 1370, 1248, 1185, 1156, 1113, 1070, 1024, 934, 838, 815, 777, 728, 700 cm^{-1} .

Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{OSi}$: C, 77.35; H, 10.82. Found: C, 77.09; H, 10.76.

2,4-Dimethyl-1-hexen-5-yn-4-ol (38). According to the general procedure, to a stirred neat sample of 2-methyl-1-tetradecen-3-yne (**33**) (41 mg, 0.200 mmol) was added $\text{H}_2\text{C}=\text{C}(\text{Me})\text{MgBr}$ (**5**) (0.47 M in THF, 1.28 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products such α,β -unsaturated ketones or an allenyl alcohol. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (29 mg, 55%) as a colorless oil.

^1H NMR δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.18-1.40 (m, 14H), 1.40-1.54 (m, 2H), 1.48 (s, 3H), 1.92 (s, 3H), 2.17 (t, $J = 7.2$ Hz, 2H), 2.25 (br s, 1H), 2.35 (d, $J = 13.2$ Hz, 1H), 2.41 (d, $J = 13.2$ Hz, 1H), 4.84 (s, 1H), 4.96 (s, 1H).

^{13}C NMR δ 14.08, 18.61, 22.66, 24.31, 28.59, 28.86, 29.10, 29.30, 29.51, 29.56, 30.47, 31.89, 51.46, 66.36, 83.97, 84.23, 115.33, 142.17.

IR (neat) 3426 (OH), 3074, 2925, 2855, 2241, 1645, 1456, 1373, 1348, 1248, 1166, 1123, 1089, 1035, 937, 892, 860, 722 cm^{-1} .

Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{O}$: C, 81.75; H, 12.20. Found: C, 81.93; H, 12.49.

2-Methyl-1-phenyl-3-tetradecyn-2-ol (39). According to the general procedure, to a stirred neat sample of 2-methyl-1-tetradecen-3-yne (**33**) (41 mg, 0.200 mmol) was added PhMgBr (**6**) (0.92 M in THF, 0.652 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products such α,β -unsaturated ketones or an allenyl alcohol. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (29 mg, 48%) as a colorless oil, .

^1H NMR δ 0.89 (t, $J = 6.6$ Hz, 3H), 1.18-1.39 (m, 14H), 1.46 (quintet, $J = 6.9$ Hz, 2H), 1.51 (s, 3H), 1.93 (s, 1H), 2.16 (t, $J = 6.9$ Hz, 2H), 2.90 (d, $J = 6.5$ Hz, 1H), 2.95 (d, $J = 6.5$ Hz, 1H), 7.23-7.34 (m, 5H).

^{13}C NMR δ 14.10, 18.61, 22.67, 28.61, 28.86, 29.14, 29.32, 29.53, 29.59, 29.89, 31.90, 49.86, 68.08, 83.55, 85.21, 126.80, 127.97, 130.74, 136.64.

IR (neat) 3397 (OH), 3086, 3063, 3030, 2925, 2854, 2242, 1604, 1496, 1456, 1373, 1248, 1165, 1123, 1089, 1031, 940, 855, 753, 700 cm^{-1} .

Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{O}$: C, 83.94; H, 10.73. Found: C, 84.15; H, 10.88.

3-[2-(Dimethylphenylsilyl)ethyl]-1-(trimethylsilyl)-1-dodecyn-3-ol (40). According to the general procedure, to a stirred neat sample of 3-nonyl-1-(trimethylsilyl)-3-buten-1-yne (**34**) (50 mg, 0.200 mmol) was added $\text{PhMe}_2\text{SiCH}_2\text{MgCl}$ (**8**) (0.93 M in Et_2O , 0.645 mL, 0.600 mmol) at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The

combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products such α,β -unsaturated ketones or an allenyl alcohol. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (73 mg, 88%) as a colorless oil.

^1H NMR δ 0.21 (s, 9H), 0.32 (s, 6H), 0.92 (t, J = 6.9 Hz, 3H), 0.93-1.03 (symmetrical m, 2H), 1.20-1.40 (m, 12H), 1.40-1.57 (m, 2H), 1.59-1.70 (m, 4H), 2.01 (s, 1H), 7.34-7.42 (m, 3H), 7.52-7.59 (m, 2H).

^{13}C NMR δ -3.14, -3.07, 0.00, 9.46, 14.09, 22.66, 24.12, 29.29, 29.50 (2 peaks), 29.72, 31.89, 36.22, 41.00, 72.68, 88.48, 108.98, 127.75, 128.87, 133.53, 138.92.

IR (neat) 3446 (OH), 3069, 3050, 2955, 2925, 2854, 2164, 1456, 1427, 1377, 1250, 1186, 1114, 1061, 998, 894, 841, 775, 760, 729, 700 cm^{-1} .

Anal. Calcd for $\text{C}_{25}\text{H}_{44}\text{OSi}_2$: C, 72.04; H, 10.64. Found: C, 71.84; H, 10.52.

Grignard Addition in the Presence of Another Dummy Grignard Reagent (entry 4, Table 4).

1-[4-(*tert*-Butyl)phenyl]-3-(trimethylsilyl)-1-propanol (42). According to the general procedure, to a stirred neat sample of *p*-(*tert*-butyl)styrene (**41**) (37 mg, 0.200 mmol) was added *n*-BuMgBr (**1**) (1.00 M in Et_2O , 0.160 mL, 0.160 mmol), followed immediately by $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (**7**) (1.15 M in Et_2O , 0.260 mL, 0.300 mmol), at room temperature under dry air. After the mixture was stirred overnight, the reaction was terminated by the addition of water (1.5 mL). The organic products were extracted with ether. The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated *in vacuo* to give a crude oil. Careful analysis of the crude product by ^1H NMR spectroscopy did not show the presence of any isomeric products. The crude product was chromatographed on silica gel (hexane-ethyl acetate) to afford the title compound (31 mg, 65%) as a colorless oil.

^1H NMR δ 0.08 (s, 9H), 0.40 (d/d/d, $J = 6.0, 11.4, 14.1$ Hz, 1H), 0.66 (d/d/d, $J = 6.0, 11.4, 14.1$ Hz, 1H), 1.33 (s, 9H), 1.64-1.84 (m, 2H), 1.94 (s, 1H), 4.55 (t, $J = 6.6$ Hz, 1H), 7.27 (d/t, $J = 8.1, 1.5$ Hz, 2H), 7.38 (d/t, $J = 8.7, 1.5$ Hz, 2H).

^{13}C NMR δ 0.87, 12.45, 31.27, 33.16, 34.41, 76.58, 125.36, 125.81, 141.77, 150.49.

IR (neat) 3375 (OH), 2954, 1654, 1248, 1014, 836, 690 cm^{-1} .

Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{OSi}$: C, 72.66; H, 10.67. Found: C, 72.40; H, 10.74.